ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Quality Water Assessment of Morava E Binçes River and Dobercan Resource (Kosovo) By Multi Elementary Analyses ICPMS and ICP/OES.

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ABSTRACT

The main objective of this research was to analyze environmental toxic elements in the water resources of Kosovo, Morava e Binçes as surface water and thermal mineral water of Doberçani as underground water. For this purpose is used very sensitive analytical methods: multi elementary analyses ICPMS and ICP/OES. The considerable amounts of environmental toxic elements inside the area of the river are continuously emitted in environment from many anthropogenic sources. Experimental results show that some parameters of water quality such as heavy metals concentration in the ground waters indicate tendency to increase compared with former experimental results. Permanent chemical monitoring of the water quality that exists in Kosovo underlines the necessity and importance of reliable potable water control to ensure that the tolerance limits for the various toxic elements are never exceeded and are under control. In the end of whole our study will be a message to authorities for preparing national waste management plan of hazardous waste and enforcement hazardous waste facilities.The mass concentrations of nickel, copper, chromium, cobalt and silver in several sample stations were over allowed concentrations in accordance with existing criteria for water quality. As first step further, surface water pollution has to be stopped and to improve the existing condition. It is necessary prevention, monitoring and reduce of scale pollution, to ensure the quality level, biological equilibrium and these water ecosystem at those places where quality rehabilitation is possible.
Keywords: Anthropogenic source, trace metals, monitoring, ICP/MS.

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ISSN: 0975-8585

INTRODUCTION

Eco-chemical elements are significant environmental pollutants, and their toxicity is a problem of increasing importance for ecological, evolutionary, nutritional and environmental reasons. Potable and safe water is gradually becoming a scarce commodity, due to mixing up of huge contaminants through natural process like soil and rock weathering and anthropogenic activities such as industrial effluents, domestic sewage, garbage, over mining activity, explosive population etc. (Gashi et al., 2011)Many ecochemical elements in natural waters are in very low level (approximately mass concentrations are less then 1μg /dm^3). Some of them are necessary bioactive and very important in many enzymatic reactions in a considerable number of living organisms. At the increase of their mass concentration, caused by result of urban and industrial wastes often exceeding the allowed limit of toxics, effectuating serious eco-physical changes in living organisms in certain localities of natural systems such as: rivers, lakes and seas (Raspor et al., 1981).To have an overview or characterize heavy metals in traces in natural water systems is very important problem and complicated to be build based on model systems. Low concentration of some chemical elements, contamination of monitored electrolytic cell, and thermodynamics of system in equilibrium are some of difficulties that comes from. For their direct characterization we need to use more sensitive analytical methods, but methods can be also used with less sensitivity if first we do concentration of the sample analysis which are often long term and lead to significant reduction in accuracy of results. To determinate molar concentrations of every chemical elements and distribution of all physical and chemical forms in traces (speciation) in natural water equilibrium resources recently will be considering as the main challenge for most of the scientists. Physical and chemical species of each element in trace are solved and distributed in the natural aquatic systems in the ionic forms (hydrated), in the form of inorganic and organic complexes or adsorbed in the colloidal particles (Florence et al., 1987). As we know natural waters contain different species of ligands with wide extension of concentrations and with traces of elements create complexes. Experimentally is proved that the influence of metal concentration in biologic processes dipends primary from the free ionic metal concentration (Omanović et al., 1994; Sunda et al., 1984). In natural equilibrium of water resources each of physical and chemical forms of metal in traces have the different toxicity. Some considerable amount of metal concentrations of aluminium, copper, cadmium, lead etc. are the most toxics but the chemical physical connection with natural ligands reduces physiologic activity, therefore their toxicity for the flora and fauna in general. Modernization and development of new analytical techniques applying very sensitive electrodes or different sensors are used successfully to detect many chemical and physical forms of metal in traces and distribution of their ionic species in the systems of natural waters(Van den Berg 1991). These methods are based on chemical physical treatment of monitored samples transforming certain metal concentrations of all forms through displacement equilibrium into free ionic metal statements, so from analytic aspect easy can be determinate (Byrne, 1996).

Uncontrolled exploring of nature assets from the human sides has caused large ecosystem pollution, endangering its existence. Sources of pollution are numerous, main ones, but not the decisive are those with chemical origin. Intensive urbanization, communication, demographic expansion, industrial waste water discharge often without preliminary treatment has consequences many hazards of ecosystem. Human resources with their activity have changed the basic composition of the atmosphere, earth and water. The contaminant materials that come from different sources, as a part of urban life, in form of gases, smoke, dust, ash, solid waste and wastewater are released to the air, water and earth. These contaminated components are of the high risk for the human health and environment (Bruland, 1983). Example, million tonnes of different granules are released in the atmosphere, as gas and steam, which make the quality of air low, particularly in some urban and industrial zones. The majority of these contaminants come back to earth and water in more dangerous form than their first time. And lots of new components coming from the human being are becoming a part of the environment. Important impact of human being on environment is the application of energy needed to increase the effectiveness of their activities. It was indicated that the growth of the world population and activation of the combustibles increase the environmental pollution (Bacaj et al., 2003). Our anthro biogeochemical cycle may be protected if we pay more attention about our concerns for degradation of environment and this research will be a data base for our country in transition about the quality of natural water resources in Kosovo as human enrichment.

Study field and methodology

Main objective of this research was to analyze some environmental toxic elements in the water resources of Kosovo, Morava e Binçes as surface water and thermal water of Dobërcani as underground water. (Grasshoff et al., 1999). During the sampling, is it pay attention that all samples present the real water quality. Also ways of receiving and transport of samples have a significant impact on the outcome of the analyses. Due to this, method of sampling is defined by International recommendations. These recommendations come from: the International Health Organization (WHO), Environment Protection Agency and U.S. States with legal acts concerned. So sampling should be done with a well planned program that earned valid results based on which we can conclude the quality of water (APHA, American Public Health Association, 1992). Samples of water are placed in clean glass container or polyethylene bottles which are cleaned first with 2-3 times with the same water from which the samples were taken. In all vessels are recorded the type of water, sample placing time, water temperature, air temperature and the name of the person who has took samples. For sample analysis are often taken sufficient 1 dm^3 of water.

Figure 1: Study area with sampling stations.

Preparation of samples in the field

The samples are taken with special bottle of one dm^3. From these bottles, are divided into four bottles of 100 cm^3 water sample, which are treated with nitric acid HNO_3 0.1mol/dm^3 to remove anions. Dry remain is dissolved again in distillate water until 100 cm^3. Following further treatment with H_2O_2 samples are evaporated in electric heater sand until complete evaporation will remove organic pollutants.

Dry residue is treated with nitric acid, left for 24 hours staying (to stabilize) and then the sample is divided into equal parts in order to analyse samples. The numbers of sampling spots is 8, and in every sampling spot were taken samples in order to determine the chemical parameters. Each sampling spot of water in the river of Morava e Binçes have been marked by codes such as: S_1, S_2, S_3, S_4, S_5, S_6, S_7 and S_8. (Gashi et al., 2012). Samples were filtrated using filter paper "Selecta" No. 589 (Germany) then is measuring pH, electric conductivity, alkalinity, hardness of water if is necessary. (Skoog et al.,1992; Alper et al.,1998).

RESULTS AND DISCUSSION

In this study project are presented chemical parameters of natural water as water enrichment and the quality of them because these resources are used for industrial purposes.

Using experimental data (Table 1, obtained by ICP-MS method), Basic statistical parameters (Mean, Geometric mean, Median, Minimum, Maximum, Variance and Standard deviation) for some elements (Stat Soft, 2001)were calculated in 8 water samples (Table 3). Also using experimental data histograms and box plot approach (Figure 2 and3) of Tukey (1977), anomalous values (extremes and outliers) for: Fe, Cd,Cu, Sb, Ni, Pb, As and Mn, in waters were determined for the whole samples. Gashi et al., 2009; 2013) Chemical analyses were used to compare the obtained amounts of the selected toxic elements (zinc, antimony, lead, arsenic, copper, cobalt, chromium, cadmium, barium and uranium) with the existing criteria for drink water quality by WHO standards, referred in further discussion. (Troni et al., 2012; 2016).

Table 1: The distribution of 40 elements determined in river water of Morava e Binçes and thermo mineral water of Doberçani with ICP/MS

Element	Method/ detection limit	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8
Na /µgdm^{-3}	ICP-MS/1	2080	1760	6820	7220	6880	12570	14220	>35000
Li/µgdm^{-3}	ICP-MS/1	1	1	4	4	4	11	17	144
Mg /µgdm^{-3}	ICP-MS/1	2760	2530	5370	6120	6010	8050	7140	>20000
Al /µgdm^{-3}	ICP-MS/2	270	300	236	428	357	475	524	544
Si /µgdm^{-3}	ICP-MS/200	4700	3800	4200	4700	4700	5100	15300	17700
K /µgdm^{-3}	ICP-MS/30	1230	1040	2090	2160	3730	4410	7540	10400
Ca/µgdm^{-3}	ICP-MS/700	12200	12400	20800	24000	32000	27000	25000	28000
Ti /µgdm^{-3}	ICP-MS/0.1	2.5	1.6	1.8	4.8	3.7	3.2	2.5	2.8
Sc /µgdm^{-3}	ICP-MS/1	1	< 1	1	1	1	2	2	4
Cr µgdm^{-3}	ICP-MS/0.5	1.5	2.1	1.7	2.4	2.3	1.6	1.8	1.2
Fe /µgdm^{-3}	ICP-MS/10	390	420	370	660	610	650	690	670
Co /µgdm^{-3}	ICPMS/0.005	0.706	0.675	0.656	0.876	0.880	0.998	0.087	0.005
Cu /µgdm^{-3}	ICP-MS/0.2	2	1.8	1.9	2.5	2.5	2.3	2.1	<0.2
Ni /µgdm^{-3}	ICP-MS/0.3	2.1	3.3	2.5	3.8	3.3	1.1	1.3	0.3
Ge /µgdm^{-3}	ICP-MS/0.01	<0.01	0.01	0.04	0.03	0.03	0.02	0.7	1.35
Mn/µgdm^{-3}	ICP-MS/0.1	69.3	76.1	86.7	105	106	66.5	97	90.6
Se /µgdm^{-3}	ICP-MS/0.2	<0.2	<0.2	0.26	0.26	0.40	0.60	0.56	0.48
Zr /µgdm^{-3}	ICP-MS/0.01	0.07	0.05	0.09	0.11	0.08	0.15	0.08	0.03
Rb /µgdm^{-3}	ICP-MS/0.005	0.682	0.58	1.66	1.84	2.66	3.40	15.7	34.3
As /µgdm^{-3}	ICP-MS/0.03	1.3	0.68	1.4	1.59	1.83	2.15	3.77	5.75
Zn /µgdm^{-3}	ICP-MS/0.5	18.8	8.6	23.8	419.8	17.9	21.4	27.5	122.6
Rb /µgdm^{-3}	ICP-MS/ 0.005	0.682	0.58	1.66	1.84	2.66	12.14	7.5	34.3
Sr/ µgdm^{-3}	ICP-MS/0.04	65.7	73.9	116	122	120	147	66.9	114
Mo/µgdm^{-3}	ICP-MS/0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.5	1.1	0.6
Cd /µgdm^{-3}	ICP-MS/0.01	0.05	0.05	0.04	0.41	0.35	0.07	0.04	0.05
Sb /µgdm^{-3}	ICP-MS/0.01	0.07	0.06	0.1	0.12	0.1	0.3	0.18	0.25
Sn /µgdm^{-3}	ICP-MS/0.1	<0.1	0.4	0.4	0.3	0.2	0.5	0.4	0.6
Cs /µgdm^{-3}	ICP-MS/0.001	0.021	0.017	0.065	0.113	0.098	0.5	0.25	17
Ba /µgdm^{-3}	ICP-MS/0.1	13.5	24.3	28.7	30.9	30.6	32.1	45.2	151
La /µgdm^{-3}	ICP-MS/0.001	0.839	0.398	0.39	0.575	0.624	0.754	0.235	0.906
Ce /µgdm^{-3}	ICP-	1.78	0.954	0.865	1.35	1.45	1.87	2.14	2.15

	MS/0.001								
Gd /µgdm^{-3}	ICP-MS/0.001	0.173	0.115	0.099	0.165	0.168	0.245	0.356	0.527
Lu /µgdm^{-3}	ICP-MS/0.001	0.006	0.005	0.005	0.007	0.008	0.04	0.07	0.052
W /µgdm^{-3}	ICP-MS/0.02	0.02	0.02	0.02	0.08	0.04	0.02	0.07	0.09
Hg/µgdm^{-3}	ICP-MS/<0.2	<0.2	0.3	0.4	0.5	0.3	0.3	0.6	0.2
Tl /µgdm^{-3}	ICP-MS/0.001	0.001	0.002	0.002	0.005	0.144	0.152	0.167	0.171
Pb /µgdm^{-3}	ICP-MS/0.01	3.68	3.86	2.49	3.24	3.4	5.64	4.27	4.12
Bi /µgdm^{-3}	ICP-MS/0.3	<0.3	0.5	0.4	<0.3	<0.3	0.7	0.5	<0.3
Th/µgdm^{-3}	ICP-MS/0.001	0.28	0.014	0.024	0.041	0.029	0.044	0.022	0.057
U /µgdm^{-3}	ICP-MS/3	0.112	0.087	0.383	0.439	0.419	0.664	0.650	0.731

The aluminum and iron mass concentrations as essential macro bioelement generally appeared to be significantly concentrated in the river water sample location S_8 (544 µgdm^{-3}) and in the river water sample location S_7 (690 µgdm^{-3}). We have come to a conclusion that this may be a direct impact from geological constitution of rocks: alluvium gravel, sand silt, limestone, maristone, calcarenite, olistoliths of cherty limestone and silty deposits. A mass concentration limits of aluminum and iron are less than 200 µgdm^{-3}respectively than 300 µgdm^{-3}according to WHO causes significant toxic effects. A mass concentration limits of manganese aremore than 100 µgdm^{-3}respectively 105 µgdm^{-3}in the sampling point S_4 and 106 µgdm^{-3} in the sampling point S_5. (The limit is 100 µgdm^{-3}according to WHO and causes significant toxic effects).

The mass concentration of cobalt was between 0.005 µgdm^{-3}(the lowest level in S_8) until 0.998 µgdm^{-3} (the highest level in sampling station S_6). The mass concentration of chromium was between 1.2 µgdm^{-3}(the lowest level in S_8) until 2.4 µgdm^{-3}the highest level in sampling station S_4). The mass concentration of the most toxic element arsenic was between 0.68 µgdm^{-3}(the lowest level in S_2) until 5.75 µgdm^{-3}(the highest level in sampling station S_7 respectively S_8). The WHO limit for arsenic is 50 µgdm^{-3}.

Table 2: The distribution of 13 elements determined in river water of Morava e Binçes and thermo mineral water of Doberçani

Element	Method	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8
Na /µgdm^{-3}	ICP /OES	208	176	468	553	484	754	854	616
Al/µgdm^{-3}	ICP/ OES	0.536	0.394	0.378	0.500	1.190	1.120	0.985	0.32
Cu/µgdm^{-3}	ICP/ OES	0.016	0.014	0.014	0.004	0.002	0.015	0.01	0.02
Co /µgdm^{-3}	ICP/ OES	0.004	0.004	0.004	0.002	0.002	0.002	0.03	0.02
Ca /µgdm^{-3}	ICP/OES	23.7	34.8	61.3	64.6	50.8	65.8	66.8	364
Mn/µgdm^{-3}	ICP/ OES	0.056	0.076	0.074	0.084	0.074	0.065	0.088	0.001
Mg/µgdm^{-3}	ICP/ OES	2.9	2.0	5.0	5.78	4.89	5.54	6.12	21.76
K /µgdm^{-3}	ICP/OES	1.44	0.987	1.656	1.845	1.664	2.145	1.978	9.35
Hg /µgdm^{-3}	ICP/OES	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Cd /µgdm^{-3}	ICP/OES	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Ni /µgdm^{-3}	ICP/OES	0.056	0.096	0.056	0.004	0.004	0.087	0.125	0.044
Cr /µgdm^{-3}	ICP/OES	0.05	0.122	0.084	0.008	0.012	0.025	0.060	0.070
Zn /µgdm^{-3}	ICP/OES	0.118	0.102	0.114	0.114	0.084	0.088	0.094	0.078

The mass concentration of the most toxic element mercury was between 0.2 µgdm^{-3}(the lowest level in S_8) until 0.6 µgdm^{-3}(the highest level in sampling station S_7). The WHO limit for mercury is 6 µgdm^{-3}. The mass concentration of copper was from 1.8µgdm^{-3} (the lowest level in S_2) until 2.5 µgdm^{-3}(the highest level in sampling stations S_4 and S_5). The mass concentration of selenium was between 0.2 µgdm^{-3}(the lowest level in S_1 and S_2) until 0.60 µgdm^{-3}(the highest level in sampling station S_6). All these eco toxic elements chromium, cobalt, copper and selenium which were under WHO allowed concentration 50 µgdm^{-3}and caused the

ISSN: 0975-8585

significant toxic effects, which were found in low concentrations. (World Health Organization Standards (2004). Guideline for drinking water quality)

Also as it belong the mass concentrations of antimony, barium, lead, thallium, zinc and uran in all water samples were under WHO allowed values. Cadmium mass concentration also appeared to be significantly concentrated in the river water. Concentrations of cadmium were under 0.2 µgdm^{-3}according to allowed values. All concentrations of every studied metals, even those on sites with anthropogenic influence, were lower than maximal allowed concentrations from WHO standards for drinking water. Concentrations of all studied metals changed irregularly alongside the course of Morava e Binçes River. This is possibly due to the natural influence of rock composition and the presence of mineralization in Karadak mountains. The decreases in element concentrations measured in the water as it looks example inside a row from table1. in some locations are likely to be due to the processes of adsorption by clay and oxide minerals, the precipitation of minerals, and changes in geologic setting.

Table 3: Basic statistical parameters for 38 variables in 8 river water samples

Variable	Descriptive statistics					
	Mean	Geo. Mean	Minimum	Maximum	Variance	Std Dev
Na /µgdm^{-3}	6456.38	3497.48	101.00	14220.00	25734925	5072.960
Li/µgdm-3	23.25	6.02	1.00	144.00	2410	49.094
Mg / µgdm^{-3}	4760.13	3075.61	101.00	8050.00	7278840	2697.933
Al / µgdm^{-3}	391.75	375.53	236.00	544.00	13946	118.093
Si / µgdm^{-3}	7525.00	6236.56	3800.00	17700.00	31247857	5589.978
K / µgdm^{-3}	4075.00	3047.97	1040.00	10400.00	11022257	3319.978
Ca/ µgdm^{-3}	22675.00	21500.99	12200.00	32000.00	51427857	7171.322
Ti / µgdm^{-3}	2.86	2.70	1.60	4.80	1	1.039
Sc / µgdm^{-3}	14.13	2.52	1.00	101.00	1233	35.118
Cr µgdm^{-3}	1.83	1.78	1.20	2.40	0	0.413
Fe / µgdm^{-3}	557.50	540.95	370.00	690.00	19164	138.435
Co / µgdm^{-3}	0.61	0.32	0.01	1.00	0	0.368
Cu / µgdm^{-3}	14.51	3.47	1.80	101.00	1221	34.947
Ni / µgdm^{-3}	2.21	1.76	0.30	3.80	2	1.237
Ge / µgdm^{-3}	12.90	0.17	0.01	101.00	1268	35.602
Mn/ µgdm^{-3}	87.15	85.93	66.50	106.00	236	15.354
Se / µgdm^{-3}	25.57	1.61	0.26	101.00	2168	46.557
Zr / µgdm^{-3}	0.08	0.07	0.03	0.15	0	0.037
Rb / µgdm^{-3}	7.60	2.96	0.58	34.30	141	11.869
As / µgdm^{-3}	2.31	1.90	0.68	5.75	3	1.658
Zn / µgdm^{-3}	82.55	34.67	8.60	419.80	19896	141.055
Rb / µgdm^{-3}	7.67	3.16	0.58	34.30	132	11.486
Sr/ µgdm^{-3}	103.19	99.02	65.70	147.00	917	30.277
Cd / µgdm^{-3}	0.13	0.08	0.04	0.41	0	0.154
Sb / µgdm^{-3}	0.15	0.13	0.06	0.30	0	0.088
Sn / µgdm^{-3}	12.98	0.76	0.20	101.00	1265	35.568
Cs / µgdm^{-3}	2.26	0.16	0.02	17.00	36	5.959
Ba / µgdm^{-3}	44.54	34.38	13.50	151.00	1928	43.905
La / µgdm^{-3}	0.59	0.54	0.24	0.91	0	0.237
Ce / µgdm^{-3}	1.57	1.49	0.87	2.15	0	0.498
Gd / µgdm^{-3}	0.23	0.20	0.10	0.53	0	0.144
Lu / µgdm^{-3}	0.02	0.01	0.01	0.07	0	0.026
W / µgdm^{-3}	0.05	0.04	0.02	0.09	0	0.030
Hg/ µgdm^{-3}	12.95	0.71	0.20	101.00	1266	35.578
Tl / µgdm^{-3}	0.08	0.02	0.00	0.17	0	0.084
Pb / µgdm^{-3}	3.84	3.74	2.49	5.64	1	0.918

Bi / µgdm^{-3}	50.76	7.21	0.40	101.00	2884	53.706
Th/ µgdm^{-3}	0.06	0.04	0.01	0.28	0	0.088
U / µgdm^{-3}	0.44	0.35	0.09	0.73	0	0.243

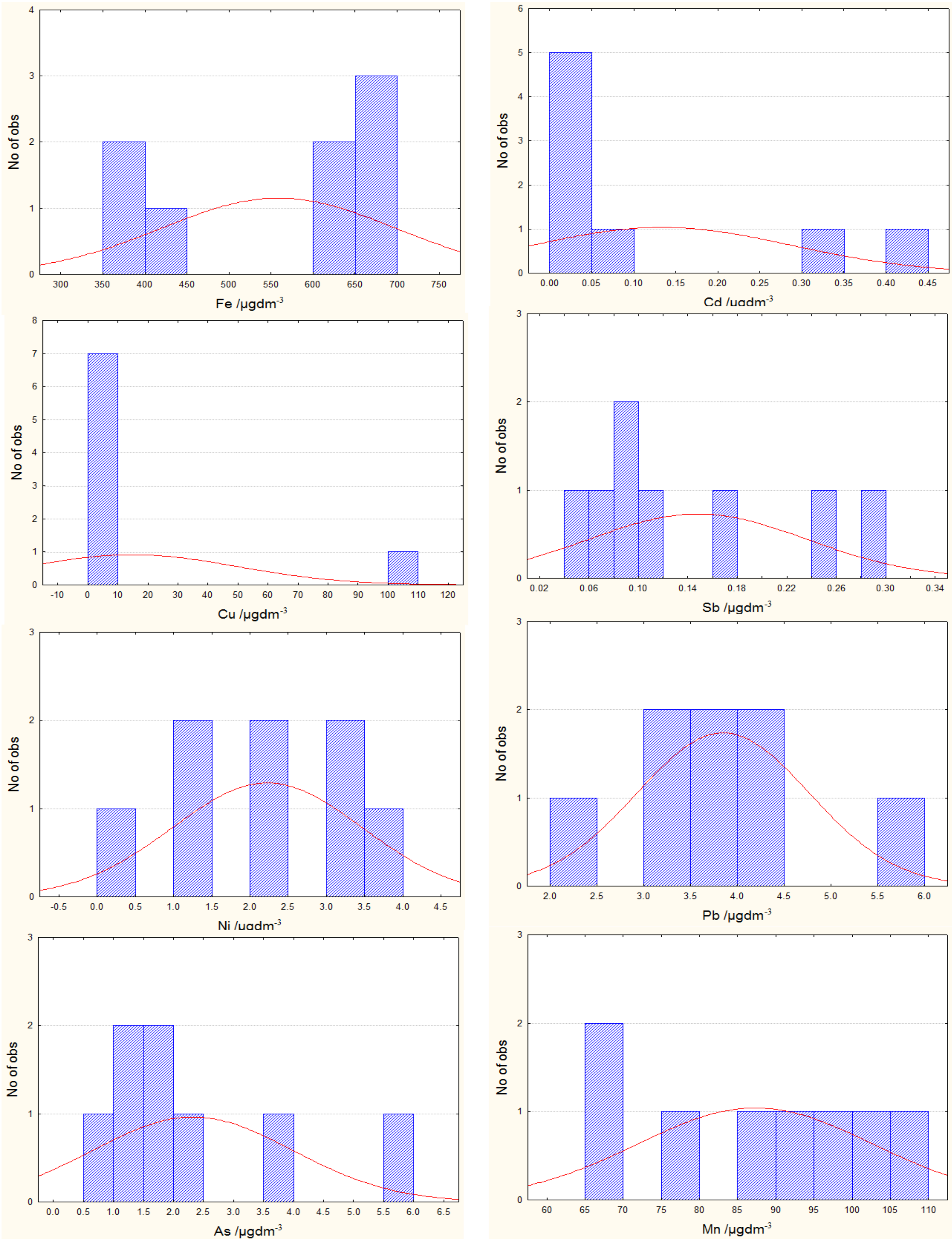

Figure 2: Histograms of 8 measured variables.

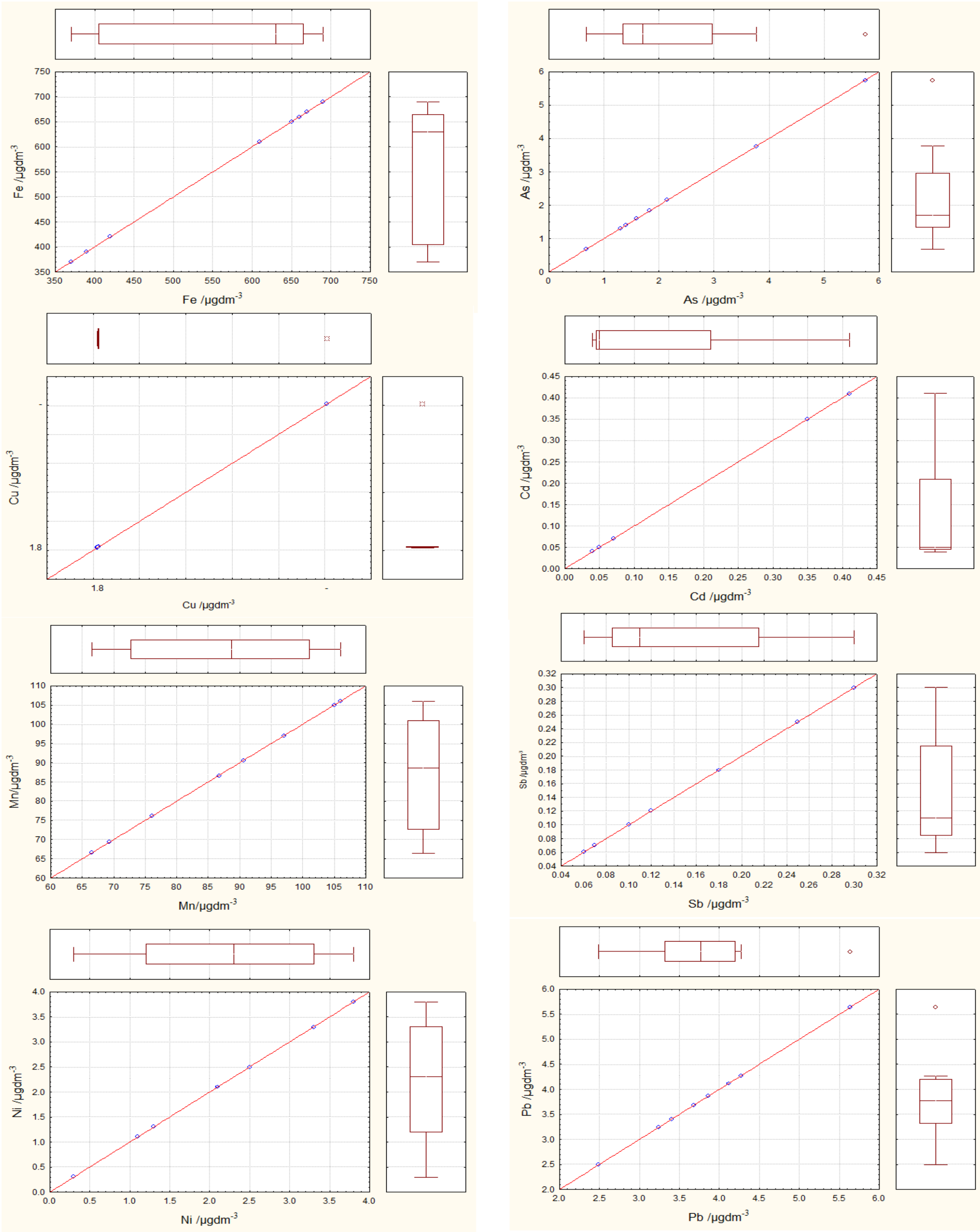

Figure 3: Scatter box plot diagrams of 8 measured variables.

Table 4: Anomalous values (extremes and outliers) determined in river waters

Sample	Extremes of parameters (¤)	Outliers of parameters (o)
S_1	No reg.	No reg.
S_2	No reg.	No reg.
S_3	No reg.	No reg.
S_4	Cu(2.5µgdm^{-3})	No reg.
S_5	Cu(2.5µgdm^{-3})	No reg.
S_6	No reg.	Pb(5.64µgdm^{-3})
S_7	No reg.	No reg.
S_8	No reg.	As(5.75µgdm^{-3})

Evaluation using two-dimensional scatter with box plots diagrams of measured metals in water samples was also performed. None of those metals shows any anomaly, and their distribution is rather irregular. An assessment of the state of heavy metal pollution of rivers is difficult as concentrations are low, and the precision of analytical results is also low. From the tables 1, we can see that calculated results in many cases we observed a variability of metal ions depending from the resource and the season where the samples were taken. In the thermo mineral water of Doberçani (monitoring in summer S_8)is evidently a high amount of mass concentration of zinc is 122.6 µgdm^{-3}, arsenic 5.75µgdm^{-3}, lead 4.12µgdm^{-3}, uran 0.731 µgdm^{-3}etc. We have to be cautious regarding these values because sometimes they are more then allowed concentrations even though they are used for medicinal purposes.

Also the mass concentrations of thallium, manganese, arsenic, cobalt and iron are flagged in red in the analyzed samples were their concentrations are evidently higher than the normal natural concentrations in water resources from the mountains. The concerns are arising because also the surface water Morava e Binçes and underground water of Doberçani are used for many industrial purposes and agricultural irrigation. These kind of natural water resorces before use must have adequate physical chemical treatment immediately. According to the results of mass concentration of macro elements in the monitoring place of Mineral water of Doberçani we could suppose that they are reached with many essential chemical elements as are calcium, magnesium, lithium iron in higher amounts with curative abilities.

The mineral water of Doberçani and similar resources before being used for human utilization like for potable water and food industry are under permanent treatment e.g. by disinfection, coagulation, flocculation, decantation, filtration, adsorption (activated carbon), disinfection (ozonisation, final chlorination), etc. Generally, the underground waters in our country are under permanent control and the fact is that laboratories for this branch of industry aren't completed with adequate equipment.

Experimental results (Tables 1.) that are shown as some characteristic parameters of water quality in monitoring place of Morava e Binçes and underground mineral water of Doberçani (winter and summer season) and are more or less in the same level compared to former experimental results. Immediately these monitored waters resorces of course are chemically treated to eliminate the eco toxic constituents with aeration methods, cationic ion exchange, deferrisation of waters with catalytic processes etc. but not enough in general. (Bacaj et all., 2003).Basic statistical parameters (Mean, Geometric mean, Median, Minimum, Maximum, Variance and Standard deviation) for some elements analyzed in 8 water samples are presented in Table 3. Based on thetwo dimensional histograms and scatter box plot diagrams (Figure 2 and 3) from experimantal data were constructed and anomalous values (extremes and outliers) were registered in Table 4. In samples S_4andS_5 extreme values of Cu(2.5µgdm^{-3})were registered. In the sample S_6 outlier value of Pb(5.64 µgdm^{-3}) was registered and in the sample S_8 outlier value of As(5.75 µgdm^{-3}) was registered as possible sign of natural pollutions.

CONCLUSIONS AND RECOMENDATION

After the water quality assessment of water resources of Morava e Binçes and underground water of Dobercani it can be concluded that these natural resources in our country are more or less "polluted" according from chemical aspects. These water resources before use for human utilization must be monitored continually and have preliminary treatment for use in the branch of industrial food.

The aluminum manganese and iron as essential macro bioelement generally appeared to be significantly concentrated in these kinds of water resources. With regard to this conclusion we consider attribution as a direct impact of geological constitution of rocks: alluvium gravel, sand silt, limestone, maristone, calcarenite, olistoliths of cherty limestone and silty deposits. All these eco toxic elements chromium, cobalt, copper mercury, arsenic and selenium which the mass concentration were under WHO Directive. Almost every studied elements changed its presence irregularly alongside the course of Morava e Binçes River and we evidenced it as impact of anthropogenic influence.

The decreases in metal concentrations measured in the water as it looks inside a row in some locations are certainly due to the processes of adsorption by clay and oxide minerals, the precipitation of minerals, and changes in geologic setting. (autopurification process).

These results as main objective intention produced from very sensitive analytical methods: multi elementary analyses ICPMS and ICP/OES to analyze trace elements of real samples are pleasant.

We must be aware regarding the gained results because sometimes we need to use equipments with high accuracy of ultra micro region of analyses as are anodic/cathodic voltammetry, dif. pulse anod. str. voltammetry, chromatographic analyses etc. that are very expensive lately.

Region of water park of Morava e Binçes, based on the results of hydro geologic research so far, possess huge quantities of thermo mineral water and dioxide carbon. In the east region part of Kosovo or alongside the Morava e Binçes there are many natural mineral and medical factories that use these waters like potable water, food industry, agronomy. etc. and has important impact in many human activities. Medical history of Thermo mineral water of Doberçani is known by many notes for therapeutic action of water thermal mineral and carbon dioxide.

Primary recommendation in general is that the surface and underground waters in our country are under permanent control but as a matter of fact our laboratories for this branch of industry aren't completed yet with adequate equipment. Despite the lack of maintenance, there is still time and potential to reduce this negative phenomenon on Kosovo's natural waters. This planed survey will be a message to authorities for preparing national waste management plan of hazardous waste and enforcement hazardous waste facilities. Prevention, monitoring and reduce of scale pollution, to ensure the quality level, biological equilibrium and in general ecosystem on these water, and at those places where quality rehabilitation is possible. Instant initiative of investment in technology fields of industrial water discharge, wastewater and urban water is necessary. These monitoring project of water worked with our students will be Study guide (Data base) for our country in transition about the quality of natural water resources in Kosovo as human enrichment.

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